

NWSC/CR/RDTR-192

AD A139634
IV

THERMAL ANALYSIS OF REACTIVITY OF PYROPHORIC
FUELS IN A CHEMICALLY SECURE ENVIRONMENT

HARLAN L. LEWIS

18 November 1982

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

Prepared for:
Commander
Naval Air Systems Command
Washington, D. C. 20361



S DTIC ELECTED APR 3 1984
A D

PREPARED BY

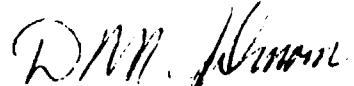
APPLIED SCIENCES DEPARTMENT

NAVAL WEAPONS SUPPORT CENTER, CRANE, INDIANA

DTIC FILE COPY

84 04 03 035

Submitted by:



D. M. JOHNSON, Manager
Chemical Sciences Branch
Research and Development Division
Applied Sciences Department

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWSC/CR/RDTR-192	2. GOVT ACCESSION NO. AD-A139 634	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Thermal Analysis of Reactivity of Pyrophoric Fuels in a Chemically Secure Environment		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Harlan L. Lewis		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Support Center (Applied Sciences Department) Crane, Indiana 47522		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N, WR02402 WR 02402002
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Weapons Support Center (Code 5063) Crane, IN 47522		12. REPORT DATE 18 November 1982
		13. NUMBER OF PAGES 12
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Naval Air Systems Command (AIR-32R) Washington, DC 20361		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES 7804G/256G		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Alloys, Pyrophoric Metals, Inert Atmosphere Enclosures		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The conditions under which air and/or moisture sensitive materials can be prepared, purified, and studied for reactivity characteristics are outlined, using the pyrophoric materials Li and Li ₇ B ₆ as examples. An experimental arrangement for examining reactivity in flowing gas atmospheres is described.		

Classification
X432
SAC
MAY 1968
A-1
Distribution/
Availability Codes
Avail 845/0
100 Specified
A-1



SUMMARY

Investigations into the modes and rates of reaction of pyrophoric solids with potential use as fuels in decoy flares are particularly difficult to conduct when it is desired to study a variety of atmospheric and temperature conditions. Sample integrity prior to exposure to a given reaction environment is also difficult to guarantee. Control of reaction rate by exposure to diluted atmospheres is also a problem.

This report provides details on a technique wherein sample preparation, handling, and exposure to a reactive environment are all completed within a secure environment. The overall system involves thermogravimetric analysis of materials in an inert atmosphere enclosure. The samples can be studied under a variety of atmospheric, changing atmospheric, and temperature conditions, with static or flowing environments with adjustable flow rates. The procedures are rapid and efficient and provide reasonable turnaround times, and they guarantee quantitative analytical information on mass change and temperature effects during the actual reaction period. Further, calorimetric data and heats of reaction under a variety of reaction conditions, and differential thermal analytic data may be easily obtained as well. Finally, the reaction products are then available for subsequent analysis for surface effects, ratios of products, etc.

The basic procedure is to effect sample preparation or synthesis in an inert atmosphere environment, transfer a measurable quantity of sample to a given thermoanalytic apparatus inside the inert atmosphere enclosure, and proceed with setting up of experimental conditions. Then the desired reactive atmosphere is introduced to an isolated sample compartment, the quantitative data gathered, and the sample compartment purged prior to recovery of the products and loading of a new sample. The procedure is quick, reliable, and completely reproducible.

PREFACE* (U)

(U) This report of NAVAIR-sponsored research consists entirely of work done at the Naval Weapons Support Center (NAVWPNSUPPCEN), Crane, and was supported by funds from AIR-32R.

* In order to specify procedures adequately, it has been necessary to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the Navy, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

TABLE OF CONTENTS

	<u>Page</u>
Summary -----	1
Preface -----	2
List of Figures -----	4
Background -----	5
Experimental -----	5
Results and Discussion -----	10
Conclusions -----	10

LIST OF FIGURES

	<u>Page</u>
Figure 1.	Diagram of Thermogravimetric Analysis Setup in the Dri-Lab. 6
Figure 2.	Reactivity of Lithium Metal with an Atmosphere of Dry Air at 175°C. 8
Figure 3.	Reactivity of Lithium Metal with Moist Ar, Triplicate Run. 9
Figure 4.	Reactivity of Lithium Metal and Li ₇ B ₆ Alloy with Atmospheres of Moist Ar or N ₂ at Ambient Temperatures. 11
Figure 5.	Reactivity of Lithium Metal and Li ₇ B ₆ Alloy with Atmospheres of Moist Air or O ₂ at Ambient Temperatures. 12

Background

Pyrophoric solids present particular difficulties for handling when it is desired to prepare, purify, and study their properties in a variety of ways. Their air-reactivity requires an inert atmosphere such as dry nitrogen or argon to be used during all manipulations. Thus, so-called dry-lab enclosures are used for their study. In situations where it is desirable to study the actual behavior of such materials in reactive environments, new problems quickly arise.

When pyrophoric materials are removed from a secure environment to the ambient world in order to perform experiments, there is a significant danger of sample contamination and degradation during all transfer operations. Then the sample integrity at the time of a test procedure is always in doubt. If, on the other hand, the reactive environment is taken to the sample and if contamination of the secure environment can be prevented, then a more reliable experimental situation prevails. Of course, there may still be difficulties associated with modifications in the reactive environment during experiments. Nevertheless, controlled, reproducible, reactive situations are desirable when it is necessary to characterize the reactive behavior of a pyrophoric material which has potential use in flare devices.

We have utilized an approach involving performance of the reaction studies in a dry-lab facility such that sample integrity is maintained prior to a reaction situation. During the actual experimental runs, the dry-lab atmosphere is secure, such that sample preparation is not threatened. Thus, samples for study can be prepared, stored, and run simultaneously in a secure environment, reproducibly, without concern for the sample integrity or for contamination of the enclosure atmosphere.

Experimental

The work to be discussed will be confined to thermogravimetric analysis (TGA) in which the mass and temperature changes in pyrophoric sample materials were observed as functions of time, when reactive gas atmospheres were introduced to the sample environment. The entire system is shown schematically in Figure 1. A Du Pont Model 951 TGA balance was used for these studies and was placed in a Vacuum Atmospheres Inert Atmosphere Enclosure which was routinely operated with an argon atmosphere, which contained less than 0.3 ppm O₂ and H₂O, and less than 3 ppm N₂. The TGA balance was connected to a Du Pont Model 990 Thermal Analysis console outside the enclosure, and all the operating conditions were controlled from the console. The mass balance was set up so that a gas flow could be maintained through the apparatus. Then a gas proportioner was used to allow rapid switchover from one sample atmosphere to another, as well as to allow mixing of two gases in any proportions. For example, a mixture of 20% O₂ in Ar could be used to simulate Air without N₂ to eliminate potential reaction conflicts with nitrogen.

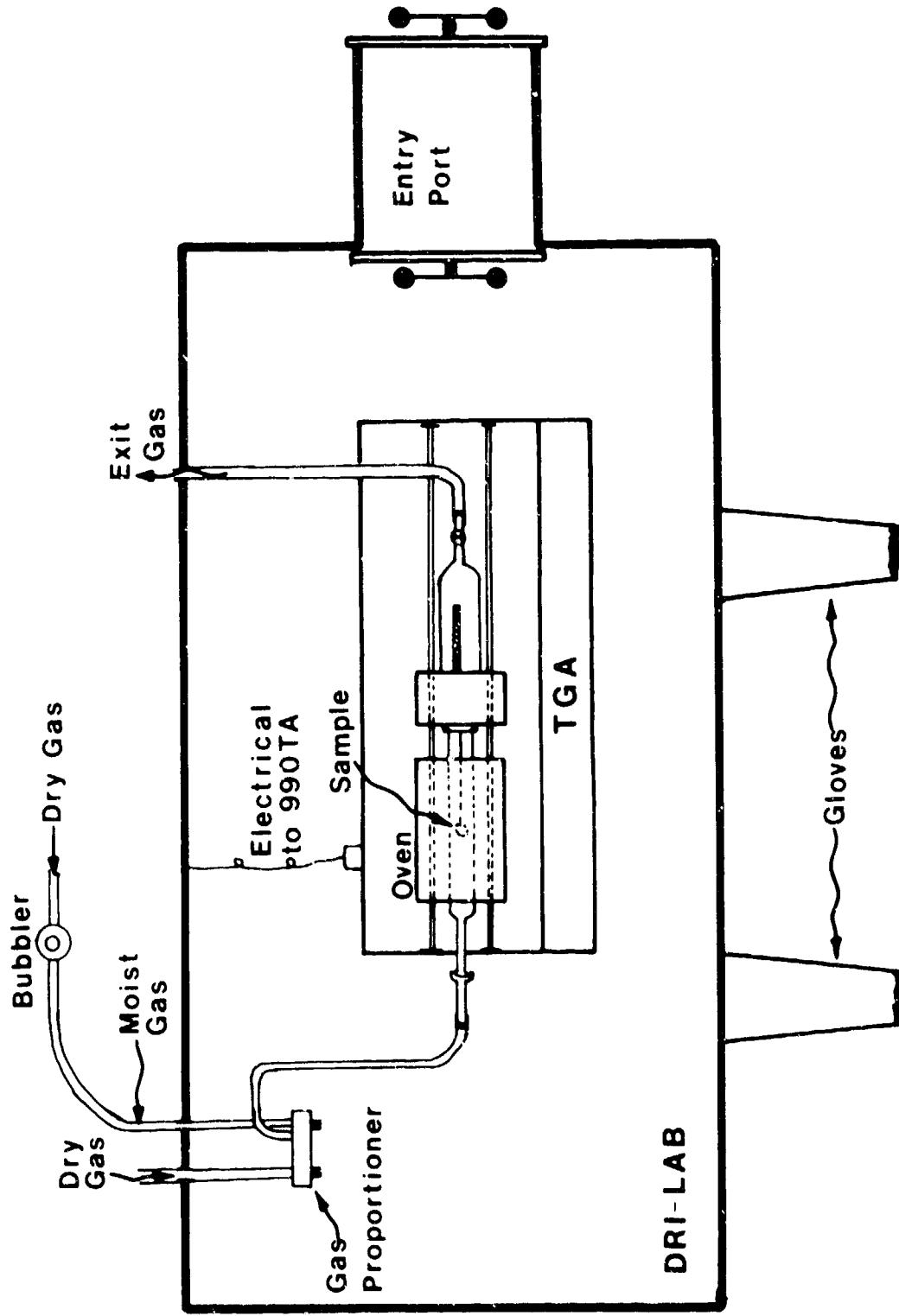


FIGURE 1. Diagram of Thermogravimetric Analysis Setup in the Dri-Lab

The sample materials to be discussed were pyrophoric: Lithium metal powder (-140 mesh) and lithium-boron alloy, Li₇B₆ (-50 mesh). Sample quantities were routinely 5-10 mg in size and were placed in a platinum pan suspended from a quartz balance arm. The loaded balance was allowed to reach equilibrium, under a flow of dry argon at about 15 ml·min⁻¹, at the desired reaction temperature. Then the reactive gas atmosphere was introduced into the apparatus, flowing also at 15 ml·min⁻¹, and mass and temperature changes with time were monitored. Typical run times were 3-4 hours, although some were much longer. The experimental arrangement also allowed the introduction of moisture into the gas flow, so that the effects of humidity on reactive atmospheres could be studied, and moisture alone in an inert gas stream could be examined.

The gases used as "dry" were Matheson Purity Air, Oxygen, Nitrogen, and Argon, with moisture contents less than 5 ppm, and the Air was CO₂ free as well. Gases used during humidity studies were just High Purity grade.

Results and Discussion

In a typical procedure, the TGA balance would be under dry Ar at the start of a run. The empty Pt pan was first tared to zero mass at the desired reaction temperature and gas flow rate. Then the balance compartment was loaded with a sample and a period of time allowed for the balance to equilibrate in the dry Ar stream. Next, the sample atmosphere was changed to the desired reactive gas. Usually, a period of 3-5 minutes was required to establish a reactive atmosphere before any indication of mass change was observed.

In Figure 2 are the data from reaction of Li metal with dry O₂ and Air, at 190°C, above the Li fusion temperature. In both gases, the reaction process occurs readily, and the data are very similar. This similarity means that Li₂O is the product from dry Air, and, therefore, that Li₃N formation is not a significant competing reaction. The slight differences in the data can be attributed to differences in gas flow rates and O₂ concentration. The significant information is the similarity in results from two experiments using different gases. The fact that the sample handling is accomplished in a secure environment allows us to infer product and reaction similarities without having to be concerned about a possible role of catalytic contaminant picked up during transfer operations of such air- and moisture-sensitive materials.

In Figure 3 are the data from three experimental runs on the reaction of Li metal powder with humid Ar. The only reactive material in such a gas flow is moisture, and the predicted final product is LiOH·H₂O. The data clearly show this product formation, along with an earlier inflection in the curves corresponding to initial formation of LiOH. Further, the data show that when the atmosphere over the sample was changed back to dry Ar, the water of hydration was quickly lost, with the product returning to LiOH. The observed mass changes correspond to:

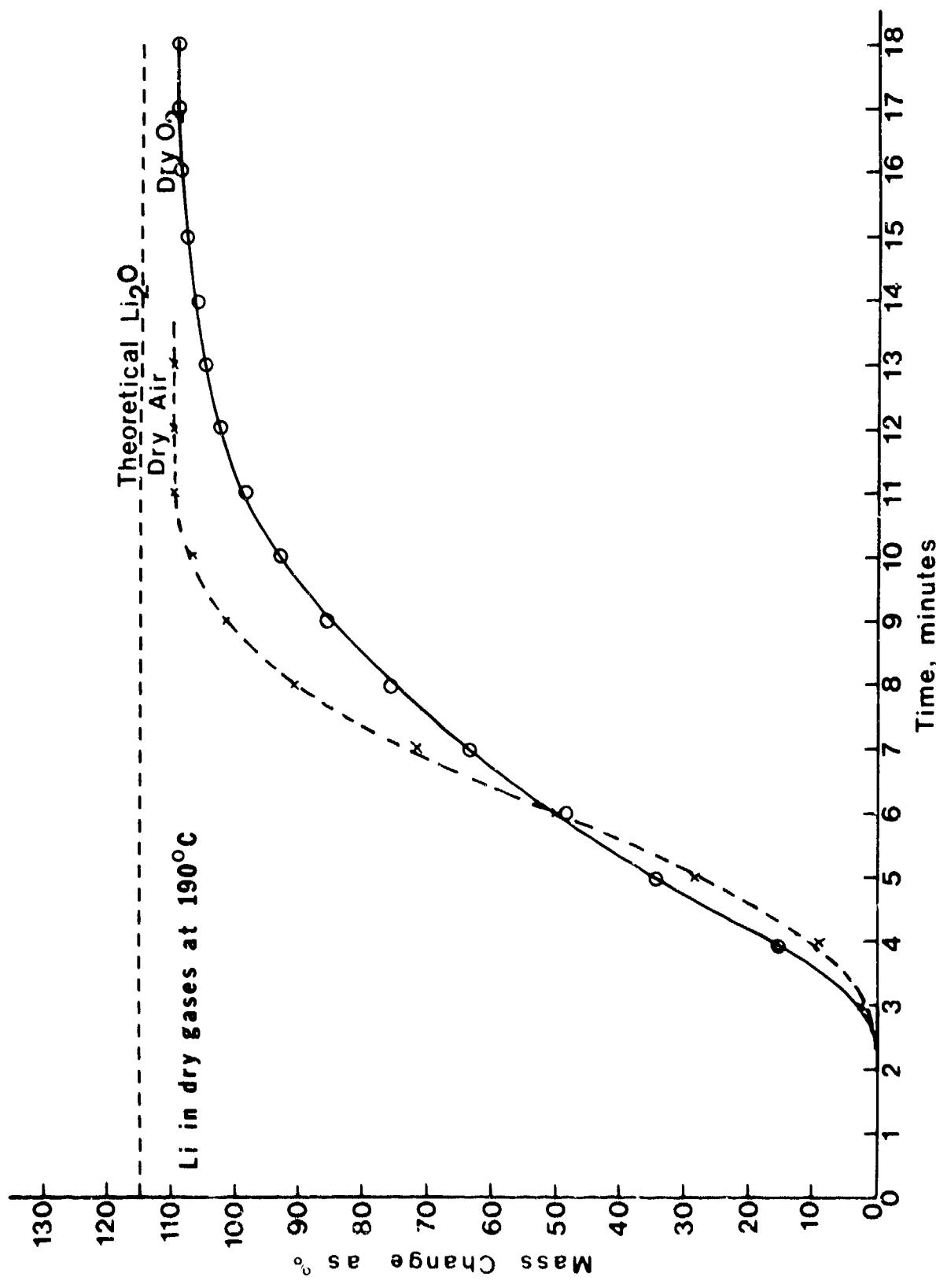


FIGURE 2. Reactivity of Lithium Metal with an Atmosphere of Dry Air at 175°C. Percent Mass Change vs. Time.

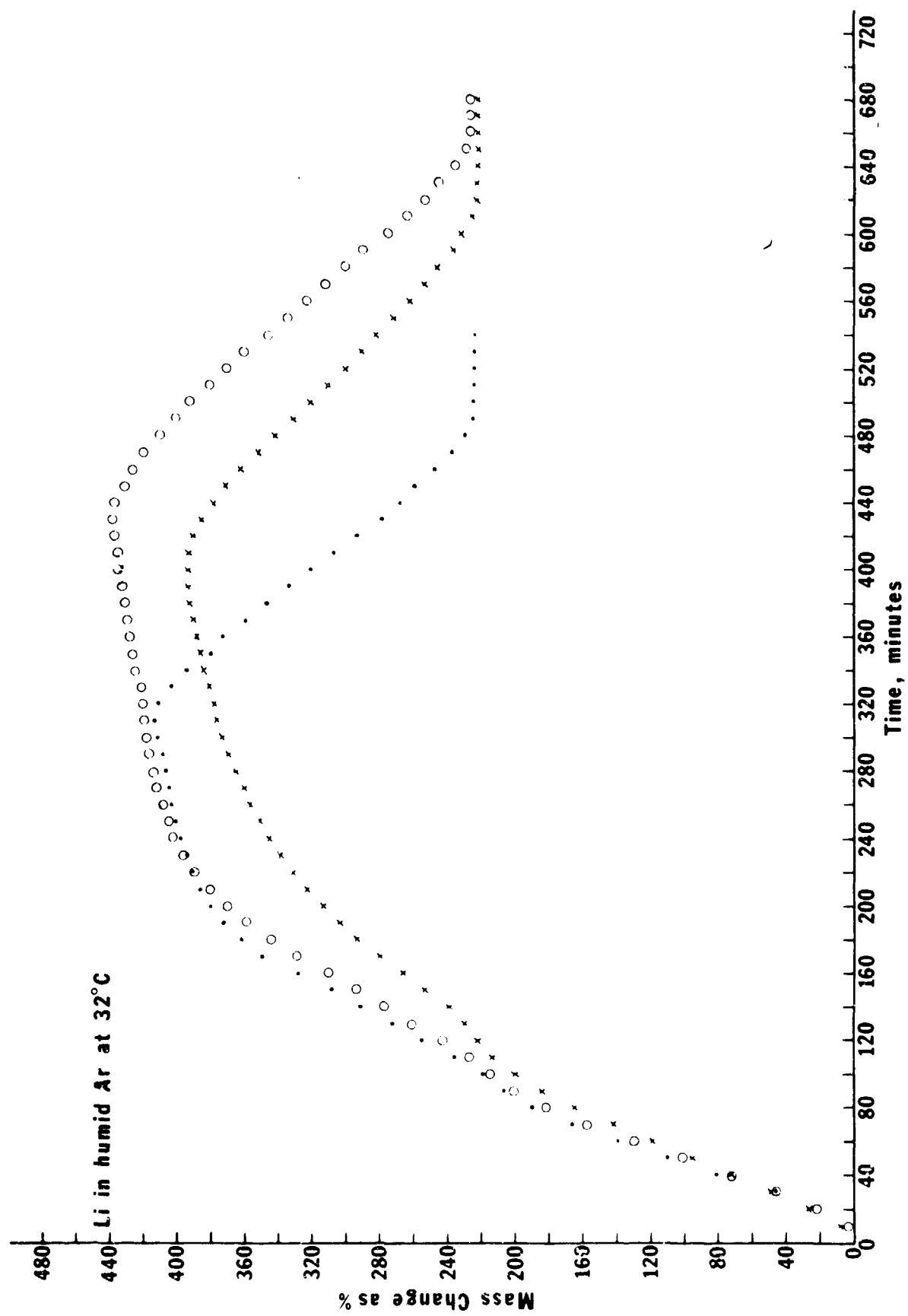
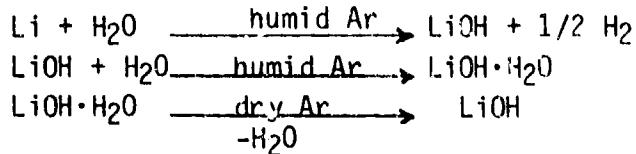


FIGURE 3. Reactivity of Lithium Metal with Moist Ar, Triplicate Run. Percent Mass Change vs. Time.



and all of this occurs readily at ambient temperature (32°C). Finally, the three runs indicate the reproducibility of the reaction processes. Thus, there is freedom from concern about sample contamination. The processes which lead to changes in sample mass must be a consequence of only the components of the atmosphere over the sample. The confidence about this fact leads in a natural way to the conclusions drawn from the data in the next two figures.

In Figure 4 are presented the data from reactions of Li metal and Li₇B₆ alloy with humid Ar and N₂, at ambient temperatures. These data allow two sets of comparisons to be made. First, it has been reported that Li₃N formation occurs readily from moisture catalyzed reaction with N₂ gas. Second, we wish to know the comparative reactivity of Li and Li₇B₆ in similar atmospheres. With regard to the first, using the data from reaction of Li metal, it seems evident that the reaction process in both atmospheres is the one outlined above in the equations. Thus, the process is formation of LiOH, conversion to LiOH·H₂O, and subsequent dehydration to LiOH in the dry Ar stream. Li₃N does not appear to form.

Next, we address the second question about the comparative reactive behavior of the two Li materials in the respective atmospheres. The data, which are in percent mass change for Li in both materials, clearly show the similarities in the behavior of the two materials. This allows us to say that Li₇B₆ behaves essentially like Li metal, that the Li component of the alloy is the reactive portion, and that its behavior at ambient temperature has been modified only slightly by incorporation into the alloy. This modification amounts to a slight reduction in overall reactivity.

Then, in Figure 5, we examine the data for the same two materials in humid Air and O₂, at ambient temperature. These data once again show that the preponderant and probably the only significant reaction is with water vapor. Lithium is simply not reactive toward O₂ or N₂ in humid environments at ambient temperatures. Also, as a consequence of the preferred reactions with H₂O, Li in both materials behaves essentially identically.

Conclusions

We have been able to investigate the reactivity of two chemically related pyrophoric materials with a variety of atmospheres and to draw conclusions about pathways and relative reactivities without concern about confusion of the data with unwanted catalytic contamination of the samples. This was achieved through the use of a secure environment in which all stages of sample preparation and study are reliable and reproducible. Thus, we can arrive at a significant understanding of the reaction processes for materials which are inherently difficult to handle, in a straightforward fashion. This understanding can then be transferred to the behavior of these materials when they are exposed to an ambient environment as they are used as fuels in flare devices.

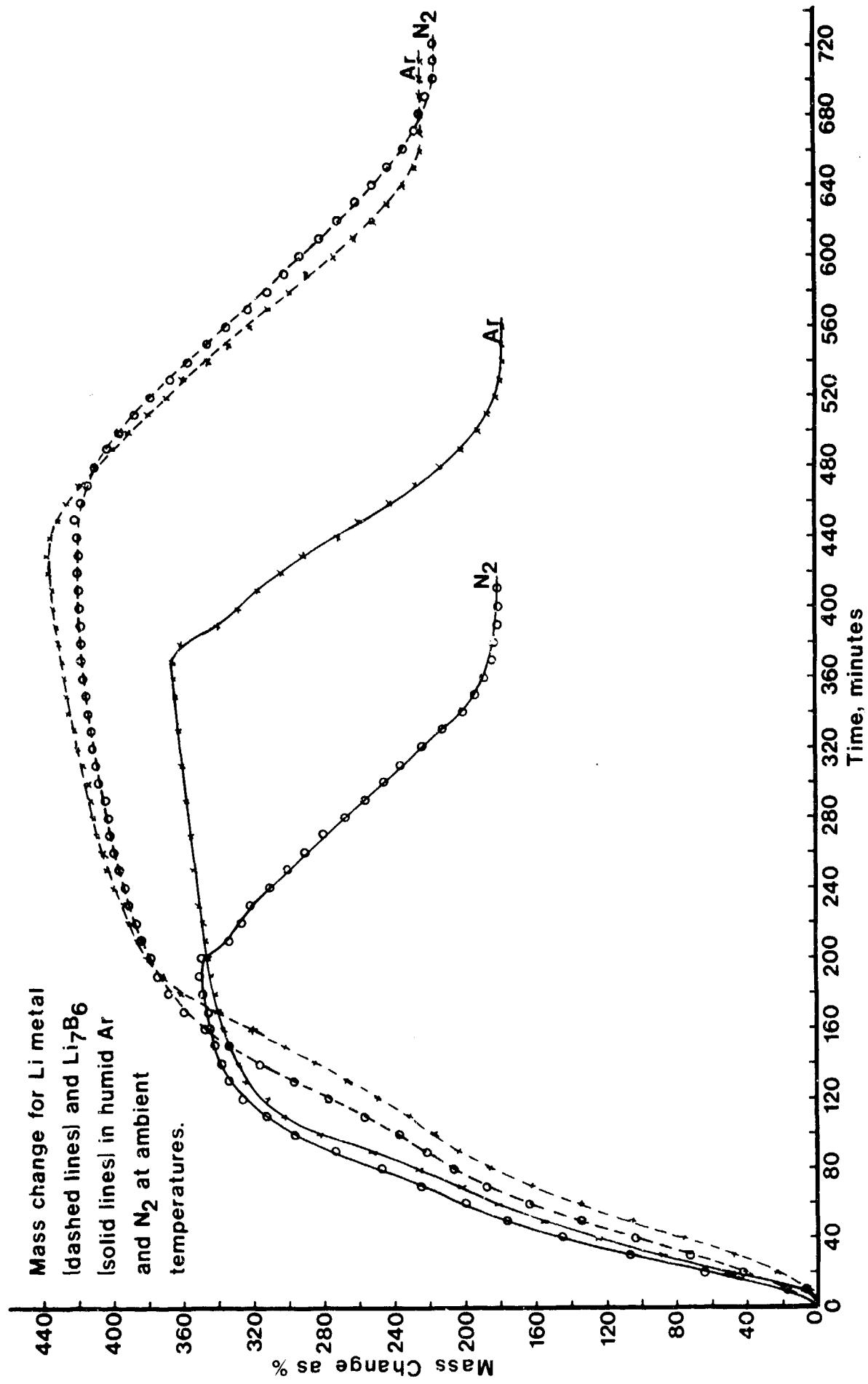


FIGURE 4. Reactivity of Lithium Metal and Li_7B_6 Alloy with Atmospheres of Moist Ar or N_2 at Ambient Temperatures.
 Percent Mass Change vs. Time.

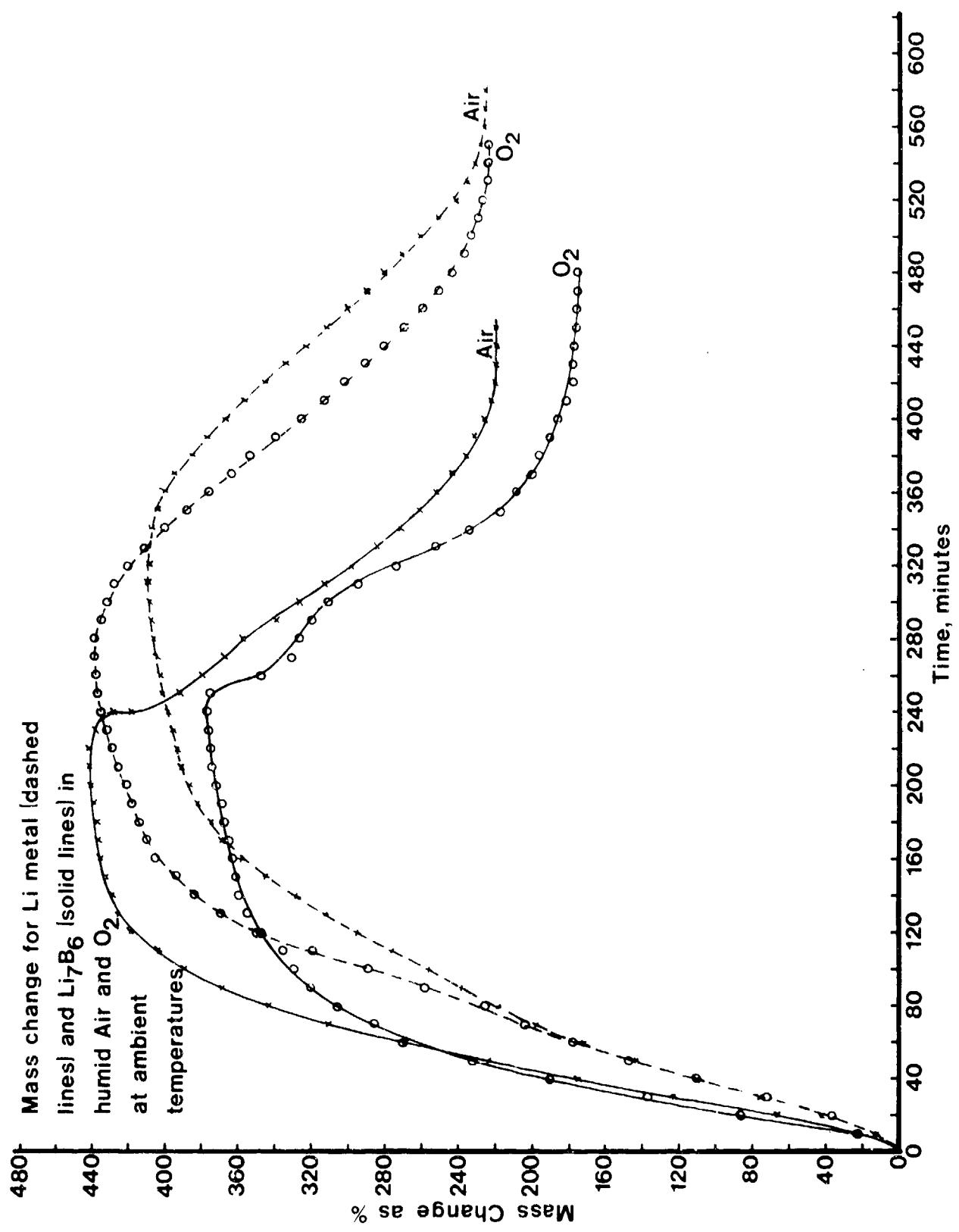


FIGURE 5. Reactivity of Lithium Metal and Li_7B_6 Alloy with Atmospheres of Moist Air or O_2 at Ambient Temperatures. Percent Mass Change vs. Time.

DISTRIBUTION LIST

1571G/12

<u>Address</u>	<u>No. Copies</u>
Administrator Defense Technical Information Center (DTIC) Cameron Station Alexandria, VA 22314	12
Headquarters U.S. Marine Corps Washington, DC 20380 Attn: Code AAW-61, LCOL F. Regan	1
Commander Naval Air Systems Command Washington, DC 20361 Attn: Code AIR-32R, Dr. H. Rosenwasser Code AIR-323B, Mr. G. Kovalenko Code AIR-54113, Mr. M. Fish Code PMA-25321, Mr. S. Bender Code AIR-954, Technical Library Code AIR-342A, Mr. P.L. Luppino Code AIP-54112 Code AIR-21531M	1 1 1 1 1 1 1 1
Commander Naval Sea Systems Command Department of the Navy Washington, DC 20362 Attn: SEA 99611, Technical Library SEA 62R32, Mr. G. Edwards SEA 65313B, Mr. W. Greenlees SEA 06R, Dr. D.J. Pastine	1 1 1 1
Commanding Officer Naval Weapons Center China Lake, CA 93555 Attn: Code 233, Technical Library Code 389, Dr. C. Dinerman	1 1
Commander Headquarters U.S. Army Armament Research and Development Command Dover, NJ 07801 Attn: Code DRDAR-TSS, Technical Library Code DRDAR-LCE-T, Mr. C. Knapp Code DRDAR-LCE-T, Mr. F. Taylor Code DRDAR-LCE-T, Mr. G. Chesnov	1 1 1 1

DISTRIBUTION LIST (CONT'D)

<u>Address</u>	<u>No. Copies</u>
Commander Air Force Armament Laboratory Eglin Air Force Base, FL 32542 Attn: Code AFATL/DLJW, Mr. A. Beach Technical Library	1 1
Commander Armament Development Test Center Eglin Air Force Base, FL 32542 Attn: Code ADTC/SDWE, Mr. S. Lander	1
Commander Rome Air Development Center Griffiss Air Force Base, NY 13441 Attn: Code RADC/IRAD, Mr. M. Manor	1
Commanding Officer Pacific Missile Test Center Electro Optics Division Point Mugu, CA 93042 Attn: Code 1233, Mr. D. Stowell Technical Library	1 1
Commander U.S. Army Electronic Command Electronic Warfare Laboratories Fort Monmouth, NJ 07703 Attn: Technical Library	1
Commanding General U.S. Army Armament Command Rock Island Arsenal Rock Island, IL 61201 Attn: Code DRSAR-RDT, Mr. R. Freeman	1
U.S. Army Foreign Science and Technology Center 220 Seventh Street, N.E. Charlottesville, VA 22901 Attn: Code DRXST-CS1, Mr. J. Jacoby	1
Commander Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910 Attn: Code X-21, Technical Library Code R-33, Dr. S. Dalleck Code R-14, Dr. G. Young	1 1 1

DISTRIBUTION LIST (CONT'D)

<u>Address</u>	<u>No. Copies</u>
Commander Naval Avionics Center Indianapolis, IN 46218 Attn: Code PC-010, Mr. P. Collignon	1
Commander Air Force Avionics Laboratory (AFSC) Wright-Patterson Air Force Base, Ohio 45433 Attn: Code AFWAL/AAWW-3, Mr. F. D. Linton Code AFWAL/AAW0-2, Mr. G. W. Schivley Code AFWAL/AAW0-2, Mr. G. W. Schivley	1 1 1
Commander Aeronautical Systems Division (AFSC) Wright-Patterson Air Force Base, OH 45433 Attn: Code ASD/AEWE/ENADC, Mr. R. Sorenson Code ASD/ENADC, Mr. H. Wigdahl Code ASD/ENADC, Mr. P. Douville Code ASD/ENAMC, Mr. G. Kunselman Technical Library	1 1 1 1 1
Chief of Naval Research Office of Naval Research 800 North Quincy Street Arlington, VA 22217 Attn: ONR 412, Dr. B.R. Junker ONR 432, Dr. R.S. Miller ONR 483, Dr. G.A. Neece	1 1 1
Commander Naval Research Laboratory 4555 Overlook Avenue, S.W. Washington, DC 23075 Attn: Code 6175, Dr. N.L. Jarvis Code 6130, Dr. R.A. DeMarco Code 6130, Dr. R.R. Smardzewski Code 5709, Mr. W.E. Howell Code 6170, Dr. H.D. Ladouceur Code 6100, Dr. D.L. Venezky	1 1 1 1 1 1